

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

### Influence of the alkyl chain length of some mesogenic molecules on their Langmuir film formation ability

Krzysztof Ingot<sup>a</sup>; Tomasz Martyński<sup>a</sup>; Danuta Bauman<sup>a</sup>

<sup>a</sup> Faculty of Technical Physics, Poznań University of Technology, 60-965 Poznań, Poland

**To cite this Article** Ingot, Krzysztof , Martyński, Tomasz and Bauman, Danuta(2006) 'Influence of the alkyl chain length of some mesogenic molecules on their Langmuir film formation ability', *Liquid Crystals*, 33: 7, 855 – 864

**To link to this Article:** DOI: 10.1080/02678290600733798

**URL:** <http://dx.doi.org/10.1080/02678290600733798>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Influence of the alkyl chain length of some mesogenic molecules on their Langmuir film formation ability

KRZYSZTOF INGLOT, TOMASZ MARTYŃSKI and DANUTA BAUMAN\*

Faculty of Technical Physics, Poznań University of Technology, 60-965 Poznań, Poland

(Received 14 October 2004; in final form 22 February 2005; accepted 26 February 2005)

Langmuir films of members of two homologous series, the 4-*n*-alkyl-4'-cyanobiphenyls (*n*CB) for  $n=2-14$  and *trans*-4-*n*-alkyl(4'-cyanophenyl)cyclohexanes (PCH*n*) for  $n=2-12$ , have been studied by recording surface pressure/area isotherms and by Brewster angle microscopy. It has been found that the compounds with very short chains ( $n \leq 3$ ) and very long chains ( $n > 12$  for *n*CB,  $n > 10$  for PCH*n*) are unable to form compressible monolayers at the air–water interface. Other members of both series can form stable Langmuir films, but both their rigidity and stability as well as the molecular packing vary with the alkyl chain length. The isotherms and BAM images imply that the organization of the liquid crystal molecules in the films is to some extent correlated with their ability to form corresponding mesophase in the bulk: nematogenic compounds tend to form rounded droplet-like domains, whereas smectogenic compounds tend to form flat domains.

## 1. Introduction

It is well documented that some thermotropic liquid crystals, whose molecules are insoluble in water and composed of a strongly polar hydrophilic head group and a hydrophobic alkyl chain, are able to form ordered monomolecular layers on an air–water interface (Langmuir films) [1–7]. Such monolayers are very simple systems in which the intermolecular interactions can be easily investigated [8]. Moreover, the air–water interface is an ideal model surface for the investigation of the way in which liquid crystal molecules are anchored to the surface, and to answer the question how the molecular alignment in the bulk is affected by surface or interfacial interactions. On the other hand, it must be kept in mind that the kind of mesophase for a thermotropic liquid crystal is normally related to the bulk. Therefore, it is interesting to explore to what extent the order in nematic and smectic phases is preserved when dealing with layers with a thickness of the order of the molecular dimension.

Previously a relationship had been found between the structure of mesogenic molecules and their ability to form stable and compressible Langmuir films [1, 7]. It was suggested that the replacement of one benzene ring of biphenyl or terphenyl core by a cyclohexane or bicyclooctane ring causes a reduction in molecular packing efficiency, making a monolayer virtually

incompressible [1]. However, our previous study [7] showed that the formation of stable monolayers on the air–water interface is determined mainly by the molecular structure of the terminal polar group, and that the structure of the molecule core (aromatic or aliphatic rings) has only a secondary effect. However, the compounds investigated in [1] and [7] are not strictly comparable since they differ in alkyl chain length. Therefore, in this paper we report a study which should help to determine whether the length of the alkyl chain has a significant effect on the ability of liquid crystal molecules to form stable and compressible Langmuir films.

We have studied Langmuir films formed by members of two homologous series: 4-*n*-alkyl-4'-cyanobiphenyls (*n*CB) for  $n=2-14$  and *trans*-4-*n*-alkyl(4'-cyanophenyl)-cyclohexanes (PCH*n*) for  $n=2-12$ . The results of the analysis of the surface pressure/mean molecular area isotherm measurements as well as Brewster angle microscope observations are presented here.

## 2. Experimental

The mesogenic 4-*n*-alkyl-4'-cyanobiphenyls (*n*CB) and *trans*-4-*n*-alkyl(4'-cyanophenyl)cyclohexanes (PCH*n*) were synthesized in Prof. R. Dąbrowski's Laboratory at the Military Academy of Technology, Warsaw (Poland). All substances were used without further purification; their phase transition temperatures (in the bulk), determined on the basis of their optical textures observed by means of hot stage polarizing microscopy,

\*Corresponding author. Email: bauman@phys.put.poznan.pl

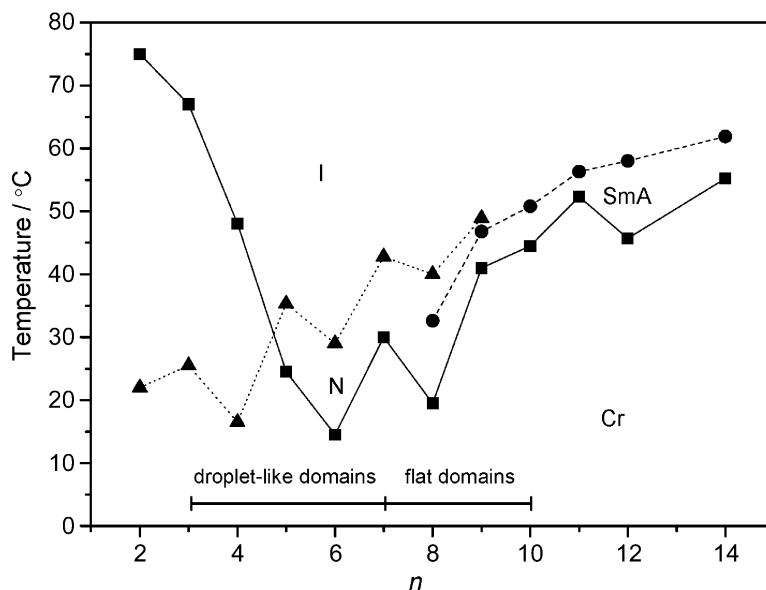


Figure 1. Phase transition temperatures for members of the  $n$ CB series.

are given in figures 1 and 2. 2CB, 3CB and 4CB show nematic phase formation only on cooling (monotropic liquid crystals); 5CB, 6CB and 7CB are enantiotropic nematogenic compounds; 8CB and 9CB have both smectic A (SmA) and nematic (N) phases, while 10CB to 14CB show only SmA phases between the solid and isotropic states. Among the compounds of the PCH $n$  series only PCH10 (monotropic) and PCH12 show the SmA phase. The SmA phase seen for members of both the  $n$ CB and PCH $n$  series is in fact the SmA<sub>d</sub> phase, because molecules form interdigitated bilayers and as a

result the distance between layers is  $\approx 1.5$  times the molecular length [9].

The mesogens were dissolved in chloroform (Uvasol, for spectroscopy, E. Merck) to stock concentrations of 0.1 mM and kept refrigerated. The solution was spread onto the deionized water subphase to form a monolayer and was equilibrated for about 15 min to allow the solvent to evaporate. The surface pressure/area per molecule experiments were carried out by means of a commercial Minitrough 2 Langmuir-Blodgett system (KSV Instruments Ltd., Finland). A Wilhelmy

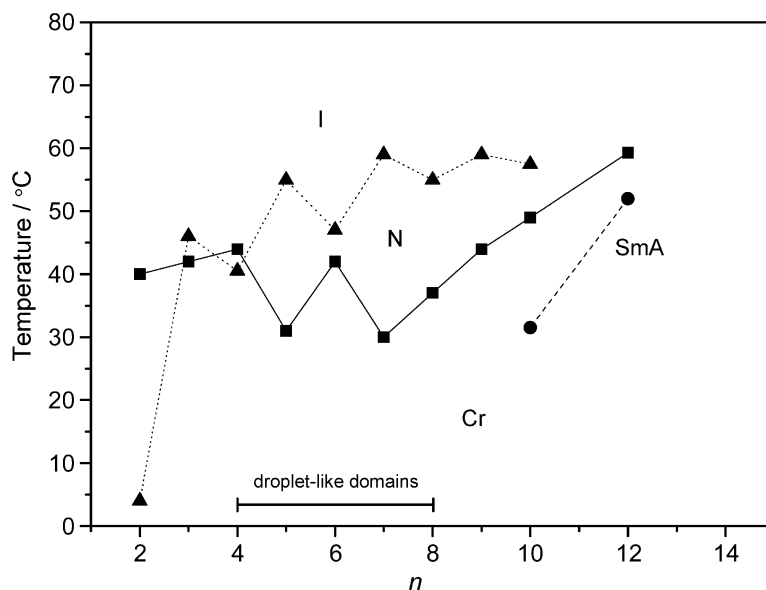


Figure 2. Phase transition temperatures for the PCH $n$  series.

platinum plate was used to measure the surface pressure with an accuracy of  $0.1 \text{ mN m}^{-1}$ . The experiments were performed at a subphase temperature of  $(23.5 \pm 0.1)^\circ\text{C}$ . Further experimental details on Langmuir film preparation are given elsewhere [10].

The morphologies of the films on the air–water interface were studied by means of a Brewster angle microscope (BAM). The instrument we used is based on the Moebius set-up [11] and was built in our laboratory. A green (532 nm) laser beam was directed at the Brewster angle ( $53.1^\circ$ ) onto the pure water. The light reflected from the monolayers was imaged by means of a CCD camera. The BAM images obtained were recorded directly on the hard disc of a PC computer, both on the continuous slow film compression and expansion simultaneously with the isotherm record. Typical reproducible images for the films at various surface pressures were saved in files using a framegrabber, then printed. The image features were observed with a lateral resolution of  $\approx 5 \mu\text{m}$ .

### 3. Results and discussion

#### 3.1. Surface pressure – mean molecular area isotherms

To obtain reference data and compare these with data given in the literature, we measured first the dependence of the surface pressure,  $\pi$ , on the average area per molecule,  $A$ , while compressing and expanding the 8CB film on the water surface. The results are given in figure 3. The compression isotherm is in excellent agreement with that already given in the literature [2, 3, 5]. The collapse point occurs at the mean molecular

area  $A=0.41 \text{ nm}^2$ , which is larger, by a factor of two, than the theoretical cross-section of an 8CB molecule ( $\approx 0.20 \text{ nm}^2$ ). This effect has been explained in terms of strong repulsive interactions between the electric dipoles of the cyano groups [2, 3]. As a result of such interactions the molecules are not densely packed, and consequently the 8CB monolayer is fragile. It was found that the average angle between the molecular long axes of 8CB and the normal to the water surface is about  $60^\circ$  [2, 12]. Thus, the alignment of the molecules in the first layer resembles a slice of the smectic C (SmC) phase rather than the SmA phase. By further compressing the 8CB film, the plateau region is observed, and at  $A=0.11 \text{ nm}^2$ ,  $\pi$  rises sharply. This value is too small for a monolayer where all the molecules remain in contact with the water surface. Xue *et al.* [2] postulated the existence of an interdigitated bilayer on top of a monolayer (trilayer) adjacent to the interface in this  $A$  region. According to de Mul and Mann [3], rigid molecular cores in the bilayer are oriented perpendicularly to the water surface, as in a SmA phase. After further compression of the 8CB film a second plateau appears suggesting the creation of the compressed multilayer assembly.

We found that under our experimental conditions with compression and expansion rates as low as  $5.0 \text{ mm min}^{-1}$ , the expansion isotherm of the 8CB film shows only slight hysteresis (figure 3), which implies that equilibrium conditions were obtained.

Figure 4 presents  $\pi$ – $A$  isotherms obtained during the compression process for chosen members of the  $n\text{CB}$  series, while the characteristic parameters of all

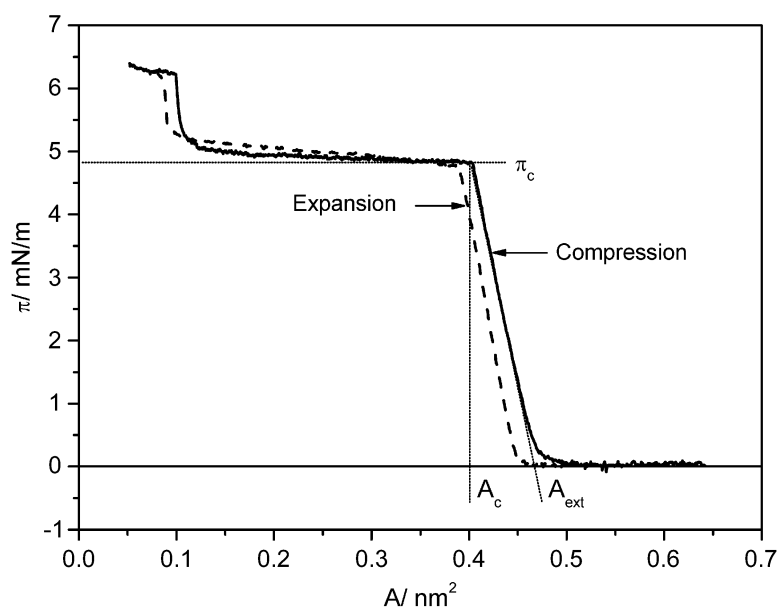


Figure 3. Surface pressure/area isotherms of an 8CB Langmuir film recorded during compression and expansion.

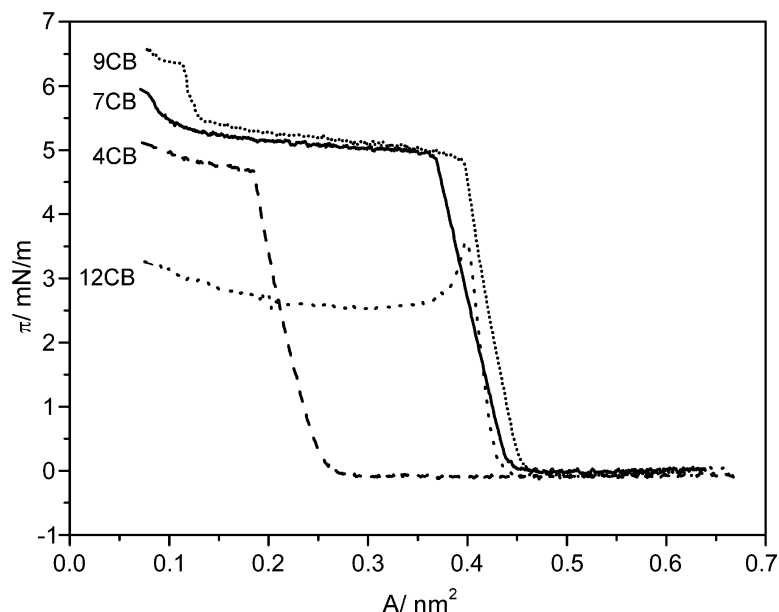


Figure 4. Surface pressure/area isotherms of Langmuir films for some members of the  $n$ CB series.

homologues of this series are given in table 1. Table 1 gathers the following data:  $A_{\text{ext}}$  is the value of the area obtained by extrapolating the steep part of the  $\pi$ - $A$  plot (the part representing the condensed monolayer creation) to  $\pi=0$  (see figure 3),  $A_C$  is the value of the collapse area, and  $\pi_C$  is the value of the collapse pressure.

From results given in table 1 it follows that 2CB, 3CB and 14CB gave monolayers which were unable to offer any significant resistance to barrier compression. Other members of the  $n$ CB series can create compressible Langmuir films, but the values of  $A_{\text{ext}}$ ,  $A_C$  and  $\pi_C$  are dependent on the alkyl chain length in the molecule. The values of the areas found from the isotherms

Table 1. Values of the area per molecule, the collapse pressure and the average angle between the normal to the water surface and rigid molecular cores for members of the  $n$ CB series.

$n$	$A_{\text{ext}}/\text{nm}^2$	$A_C/\text{nm}^2$	$\pi_C/\text{mN m}^{-1}$	$\delta_{\text{av}}/^\circ$
2	—	—	0	—
3	—	—	0	—
4	0.26	0.19	4.7	24
5	0.41	0.33	5.0	45
6	0.45	0.37	5.3	54
7	0.42	0.36	5.0	51
8	0.46	0.41	4.8	61
9	0.45	0.40	4.8	59
10	0.45	0.41	5.0	62
11	0.44	0.39	5.5	59
12	0.45	0.41	4.6	62
14	—	—	0	—

suggest that in the monolayer formed of all the compounds, the rigid cores of the molecules must be tilted with respect to the water surface. Assuming that the mean molecular area in the Langmuir film is determined by the rigid core of the liquid crystal molecule and taking the experimental  $A$  value into account, it is possible to calculate the tilt angle. Table 1 gives the values of the angle  $\delta$  estimated as the angle between the long axis of the rigid molecular core of 4CB–12CB and the normal to the water surface in the vicinity of the collapse point. It is seen that this angle depends to some extent on the alkyl chain length and, with the exception of 4CB, is rather high. This means that the liquid crystal molecules are significantly tilted away from the normal to the water surface. It is worth noting that the value of  $\delta$  for 8CB obtained in our experiment is in agreement with the value obtained previously [2, 12]. The molecular packing, and thereby the vertical alignment, is significantly higher for 4CB than for  $n$ CB with more than 4 carbons in the alkyl chains. Similar results were obtained previously for Langmuir films formed of some perylene-like compounds [13]. Moreover, from results shown in figure 4 and table 1 it follows that although the steepness of the  $\pi$ - $A$  isotherm for  $n$ CB compounds increases with increasing alkyl chain length, indicating some improvement of the monolayer rigidity, the collapse pressure does not change significantly.

The relationship between the appearance of the appropriate liquid crystalline phase for  $n$ CBs in the bulk (figure 1) and the ability for Langmuir film

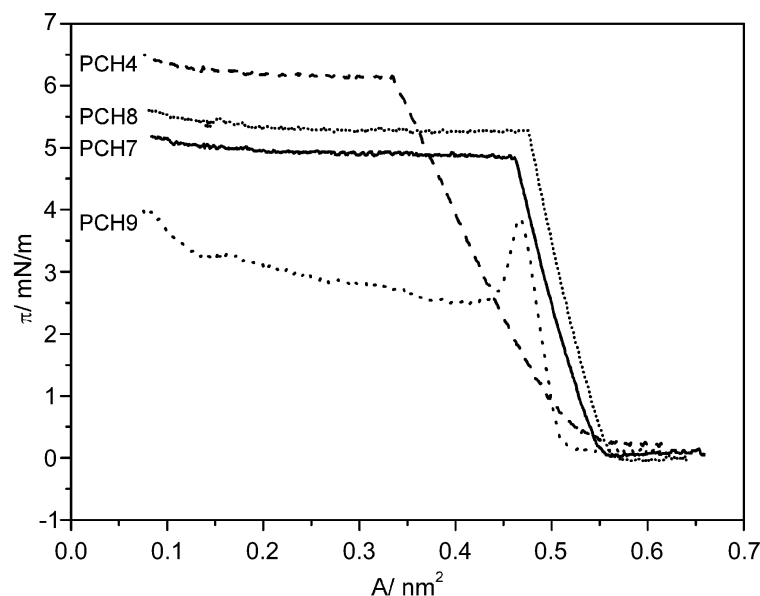


Figure 5. Surface pressure/area isotherms of Langmuir films for some members of the PCH $n$  series.

formation is not clear, but it seems that some correlation is present. Compressing the monolayer formed of 4CB, 5CB and 6CB below  $A=0.11 \text{ nm}^2$ , it is not possible to obtain a rapid rise of  $\pi$  and then a second plateau, as it was observed for 8CB (figure 3), although the pressure value increases somewhat. For 7CB a small second plateau is obtained but the rise of  $\pi$  is less rapid and distinct (figure 4). In contrast, the  $\pi$ - $A$  isotherm shapes of 9CB and 10CB are almost identical to that of 8CB. Similar results were obtained by de Mul and Mann [4], although they ascertained on the basis of BAM observations that the multilayered structures were in a metastable state. The isotherms for 11CB and 12CB have a qualitatively different form from those recorded for the previous members of the  $n$ CB series. They show a 'spike', *i.e.* a rapid fall of the surface pressure after the collapse point. This indicates that the alkyl chains in 11CB and 12CB molecules are too long to maintain the stability of the Langmuir film. Nevertheless, it can be concluded that, provided the alkyl chain is not too long, the smectic phase occurring in the bulk is conducive to the creation of a regular multilayer on the water surface.

The results of the surface pressure *versus* mean molecular area measurements for Langmuir films formed of the members of the PCH $n$  series are given in figure 5 (for PCH4, PCH7, PCH8 and PCH9) and in table 2. The data indicate that here, as in the case of the  $n$ CB series, the members with very short or very long alkyl chains are unable to form compressible monolayers on the air-water interface. Non-zero  $\pi_C$  values were obtained only for liquid crystals with  $n=4$ -10. The character of  $\pi$ - $A$  isotherms for these members of the

PCH $n$  series is quite similar to that for all the members of the  $n$ CB series up to  $A \approx 0.10 \text{ nm}^2$ . After the collapse point, the surface pressure shows a broad plateau. However, for any compound from the PCH $n$  series the second distinct rise of  $\pi$  and the plateau related to the homogeneous trilayer creation were not observed. This fact seems to be confirmation of the previous statement that only smectogenic molecules are able to form a regular multilayer in a Langmuir film. Similarly, as in the case of the  $n$ CB series, the rigidity of the monolayer fabricated from the PCH $n$  series compounds increases with increasing alkyl chain length, and the molecular packing is the highest for the member with  $n=4$ .

$\pi_C$  remains almost constant for PCH4 - PCH8. For PCH9 and PCH10 the  $\pi$ - $A$  isotherms show a 'spike', as in the case of 11CB and 12CB, indicating that already

Table 2. Values of the area per molecule, the collapse pressure and the average angle between the normal to the water surface and rigid molecular cores for members of the PCH $n$  series.

$n$	$A_{\text{ext}}/\text{nm}^2$	$A_C/\text{nm}^2$	$\pi_C/\text{mN m}^{-1}$	$\delta_{\text{av}}/^\circ$
2	—	—	0	—
3	—	—	0	—
4	0.52	0.34	6.1	36
5	0.58	0.46	5.5	52
6	0.54	0.44	5.6	50
7	0.55	0.46	4.8	53
8	0.56	0.48	5.3	54
9	0.51	0.47	3.9	53
10	0.51	0.48	3.0	55
12	—	—	0	—

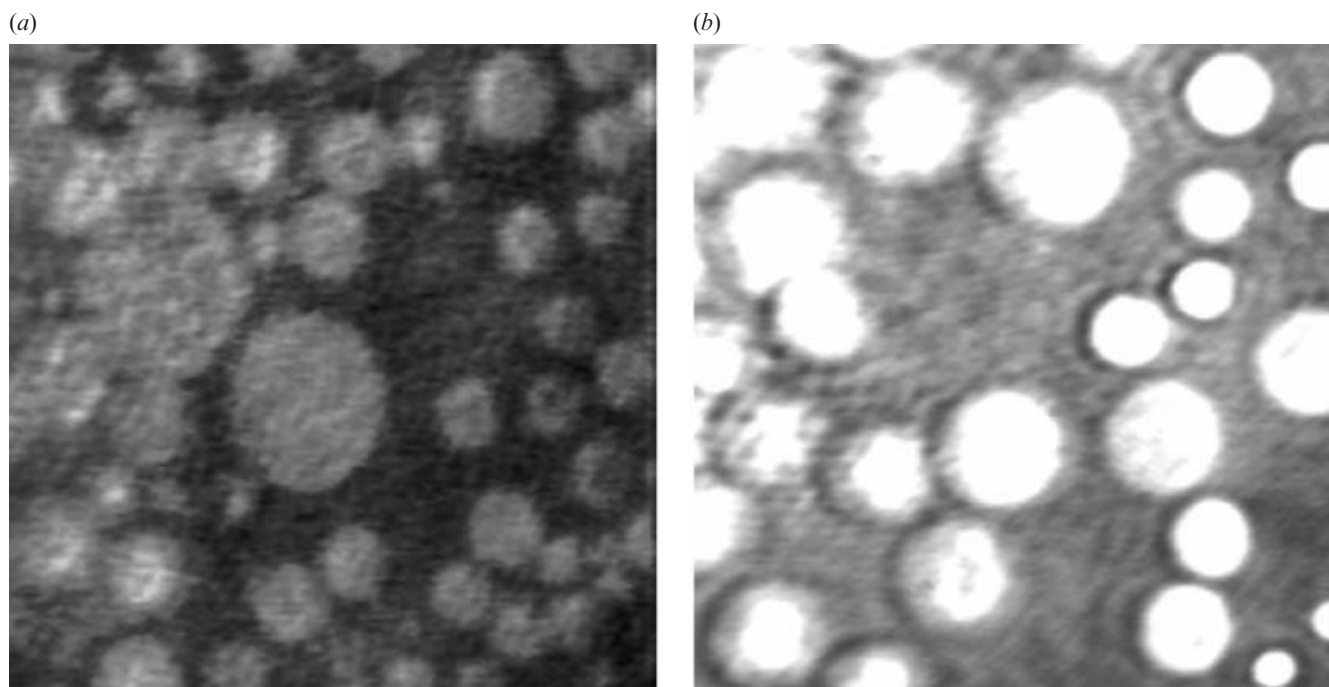


Figure 6. BAM images of an 8CB Langmuir film at mean molecular areas (a)  $A=0.25 \text{ nm}^2$  and (b)  $A=0.06 \text{ nm}^2$ . The area of images is  $0.14 \times 0.18 \text{ mm}^2$ .

the alkyl chain with 9 carbon atoms is too long to keep the Langmuir film stable. The  $\pi$ - $A$  isotherms presented in figure 5 and the data listed in table 2 show that Langmuir films created from the liquid crystals of the PCH $n$  series have higher  $A_{\text{ext}}$  and  $A_C$  values than those of the Langmuir films of the corresponding  $n$ CB compounds. This does not necessitate a lower molecular packing, because the cyclohexane ring is much bulkier than the benzene ring affecting the surface of the molecular core. As a result, the angle  $\delta$  for a given member of the PCH $n$  series is smaller than that for the equivalent member of the  $n$ CB series, except for the compounds with  $n=4$ . In the latter case a more vertical alignment for the member of the  $n$ CB series was found. Generally, the angles  $\delta$  for PCH $n$  molecules differ from those for corresponding  $n$ CB molecules by no more than 15%. Other conclusions about the difference in molecular alignment of various compounds on the air-water interface can be drawn on the basis of a BAM images analysis.

### 3.2. Brewster angle microscopy images

Brewster angle microscopy allows the direct observation of the morphology of Langmuir films. Imaging of the surface film was performed for all the liquid crystals investigated, at different surface pressures  $\pi$  during a slow continuous film compression and expansion.

BAM images of the 8CB film recorded by us were similar to those in the literature [3, 5]. In the region of coexistence of the gas and liquid phases (submonolayer), we observed condensed monolayer islands in equilibrium with a foam-like structure. As the surface pressure was raised, the islands packed together into an unbroken monolayer, giving a homogeneous picture. Just after the collapse point in the first plateau region, small brighter circular domains were observed, and these grew with reduction of the film area. Figure 6(a) presents a BAM image of the Langmuir film formed of 8CB at  $A=0.25 \text{ nm}^2$  (first plateau region of  $\pi$ - $A$  isotherm) during compression. By further reduction of the available area, when the domains observed became sufficiently large, they deformed and coalesced, as the stress at the domain boundary lines crossed a threshold value. Collapsed domains of 8CB in the plateau region appeared to be of homogeneous reflectivity, indicating that they have equal thickness. Thus, we observed the transition from a uniform monolayer to a uniform multilayer. At the second rise of  $\pi$ , a compressed multilayer structure (trilayer: monolayer covered by interdigitated bilayer, according to [2, 3]) was created, and by further compression (second plateau region), new circular domains were formed, which are shown in figure 6(b) ( $A=0.06 \text{ nm}^2$ ).

BAM images similar to those for 8CB were obtained for 9CB and 10CB in the whole region of  $A$ . However,



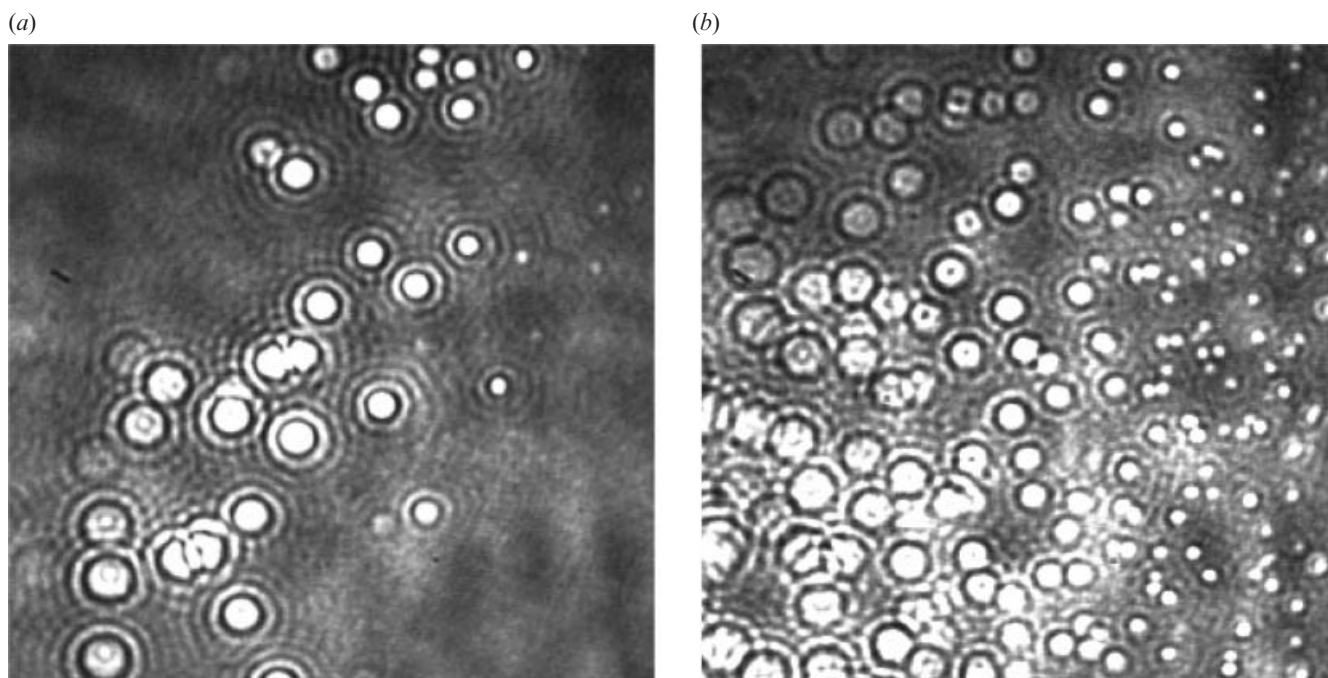


Figure 7. BAM images of a 5CB Langmuir film at mean molecular areas (a)  $A=0.25 \text{ nm}^2$  and (b)  $A=0.10 \text{ nm}^2$ . The area of images is  $0.35 \times 0.30 \text{ mm}^2$ .

BAM images for 4CB and 5CB were similar to those of 8CB only up to the collapse point. For compression beyond this point, we observed the appearance of domains of much higher brightness surrounded by interference rings. As examples, figure 7 presents BAM images of the Langmuir film formed from 5CB at  $A=0.25 \text{ nm}^2$  (a) and  $A=0.10 \text{ nm}^2$  (b) during compression. It can be seen that with the decrease of  $A$  the number of domains rises. However, they are not in collision and do not fuse. The higher brightness of the domains in comparison with those observed for 8CB–10CB indicates that they are thicker. The rings, however, are due to the interference of the light beams reflected from the air–domain and domain–water interfaces (Newton rings). The detailed analysis of the rings structure suggests that the domains grow in the third dimension when  $A$  decreases. This leads to the conclusion that we are dealing with 3D objects.

The behaviour of the Langmuir films formed from 6CB and 7CB is intermediate between that of 8CB–10CB and that of 4CB and 5CB films. Up to  $A \approx 0.14 \text{ nm}^2$ , domains characteristic of 8CB–10CB are observed, indicating the formation of a bilayer on top of a monolayer. However, further compression caused the creation of objects very similar to those found for 4CB and 5CB. This is illustrated in figure 8 for 6CB at  $A=0.14 \text{ nm}^2$ . In the BAM image shown here the existence of both kinds of domain is distinctly seen.

Figure 9 shows BAM images for PCH8 (a) at  $A=0.25 \text{ nm}^2$  obtained during compression and (b) at  $A=0.60 \text{ nm}^2$  recorded after expansion. The images presented illustrate that the behaviour of a PCH8

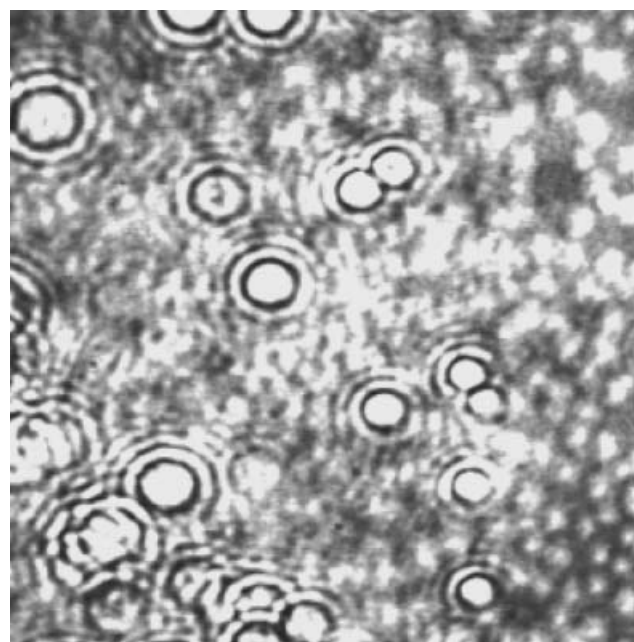


Figure 8. BAM image of a 6CB Langmuir film at mean molecular area  $A=0.14 \text{ nm}^2$ . The area of the image is  $0.35 \times 0.30 \text{ mm}^2$ .



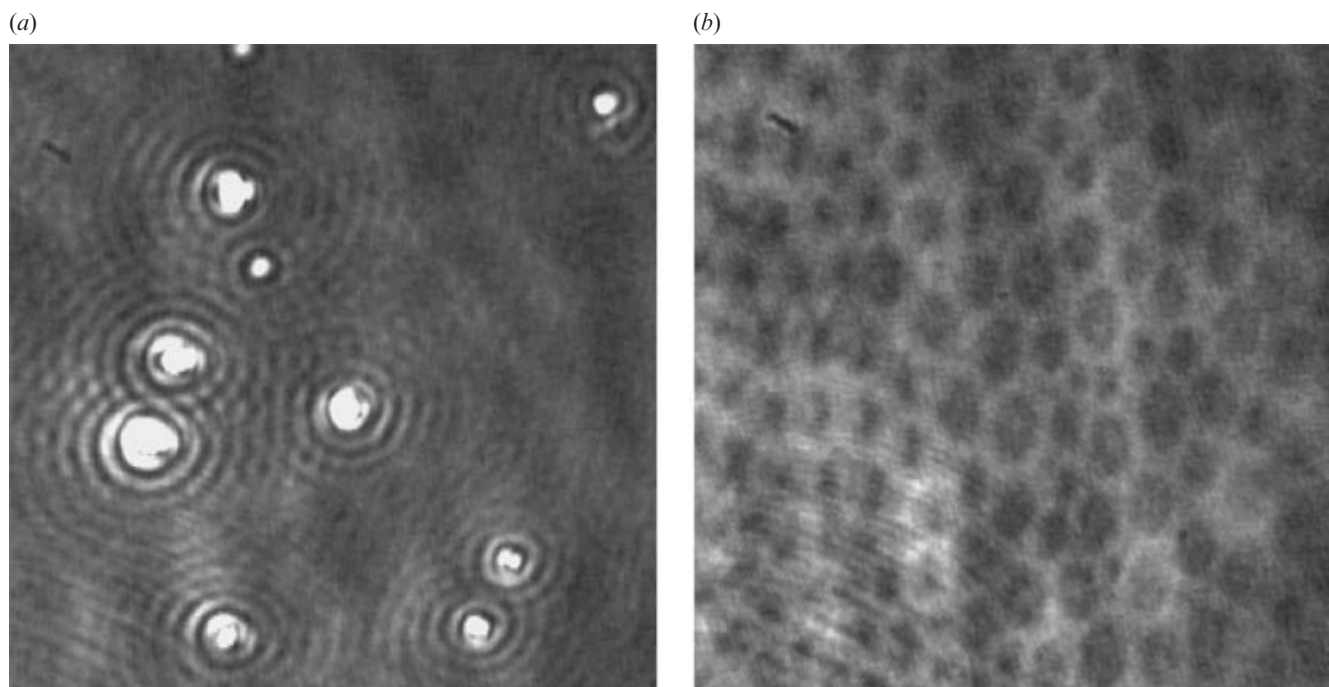


Figure 9. BAM images of a PCH8 Langmuir film at mean molecular areas (a)  $A=0.25 \text{ nm}^2$  and (b)  $A=0.60 \text{ nm}^2$ . The area of images is  $0.25 \times 0.20 \text{ mm}^2$ .

monolayer is similar to that characteristic of 4CB and 5CB. The BAM results obtained for other PCH $n$  members indicate that the monolayers formed of these liquid crystals on the water surface do not differ in character from that of PCH8.

Our observations seem to suggest that the shape and character of the domains observed beyond the collapse point can be related to the liquid crystalline phase which the compounds form in the bulk. Previously, Suresh and Bhattacharyya [14] investigated the 8CB monolayer on a water surface at different temperatures using a fluorescence microscope. At temperatures corresponding to the existence of the SmA phase in the bulk they observed optically flat domains representing a 'trilayer' phase (first plateau region of  $\pi$ - $A$  isotherm) or a regular 'multilayer' phase (second plateau region). Under similar conditions, BAM studies on 8CB revealed the images presented in figure 6 and in [3, 5]. With an increase of temperature above the SmA-N transition, instead of multilayer domains, the lens-shaped domains appeared. These lens-like 3D domains were observed also at temperatures corresponding to the isotropic phase in the bulk. Suresh and Bhattacharyya [14] postulated that 8CB monolayer domains for  $A$  less than  $0.20 \text{ nm}^2$  exhibit different phases depending on temperature. At temperatures below  $28^\circ\text{C}$  (near the SmA-N transition in the bulk) they are flat and have SmA $_d$  order. Next they become

lens-shaped with a nematic order. At higher temperatures the domains contain molecules with isotropic arrangement. The BAM images obtained in this work appear to confirm the conclusions drawn from fluorescence microscopy. Our studies show that some correlation exists between the molecular organization of liquid crystals on the air-water interface in the plateau region of the  $\pi$ - $A$  isotherm and their ability to create the corresponding phase in the bulk: smectogenic compounds tend to form flat domains containing molecules aligned in an interdigitated bilayer, whereas nematogenic compounds tend to form rounded droplet-like domains, in which the molecules can have nematic order. The suggested molecular organization in these flat and droplet-like domains is depicted schematically in figure 10.

Figure 11 shows BAM images (a) for 12CB at  $A=0.25 \text{ nm}^2$  and (b) PCH9 at  $A=0.15 \text{ nm}^2$  during compression. It is seen that in the case of compounds which are unable to form a stable Langmuir film beyond the collapse point, the BAM images can be very different. In the case of 12CB domains resembling crystallites were observed, whereas in the case of PCH9 hair-like objects were found.

#### 4. Conclusions

The surface pressure/area ( $\pi$ - $A$ ) dependence for Langmuir films formed from liquid crystals of two

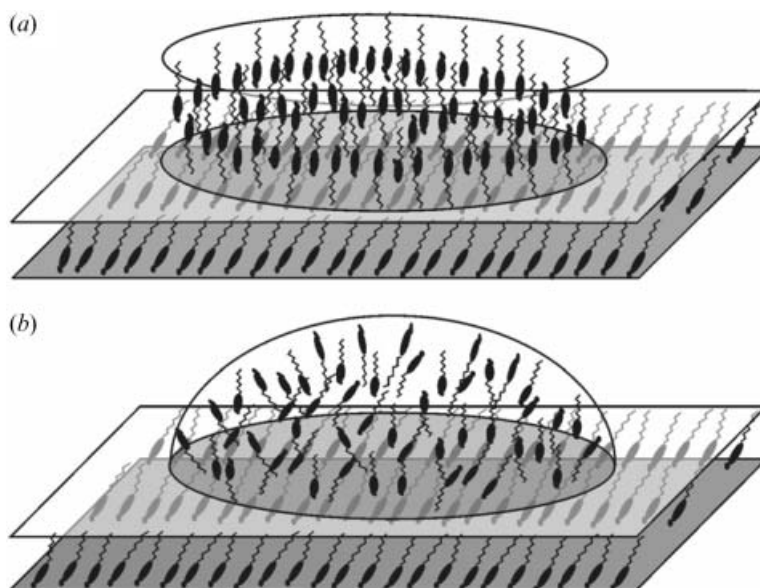


Figure 10. Schematic representation of molecular organization in (a) flat and (b) droplet-like domains.

homologous series, 4-*n*-alkyl-4'-cyanobiphenyls ( $n=2-14$ ) and *trans*-4-*n*-alkyl(4'-cyanophenyl)cyclohexanes ( $n=2-12$ ), has been studied. The homologues with very short or very long alkyl chains were unable to form a compressible monolayer on the water surface, a similar trend to that observed for the fatty acid series with varying alkyl chain length [8, 15]. Other members of the

*n*CB and PCH*n* series form compressible Langmuir films, and the shape of the  $\pi$ - $A$  isotherm is dependent on the alkyl chain length. It has been found that the rigidity of the film shows a tendency to increase with increasing alkyl chain length, whereas the stability remains more or less constant. The molecular packing depends also on the alkyl chain length and, in principle,

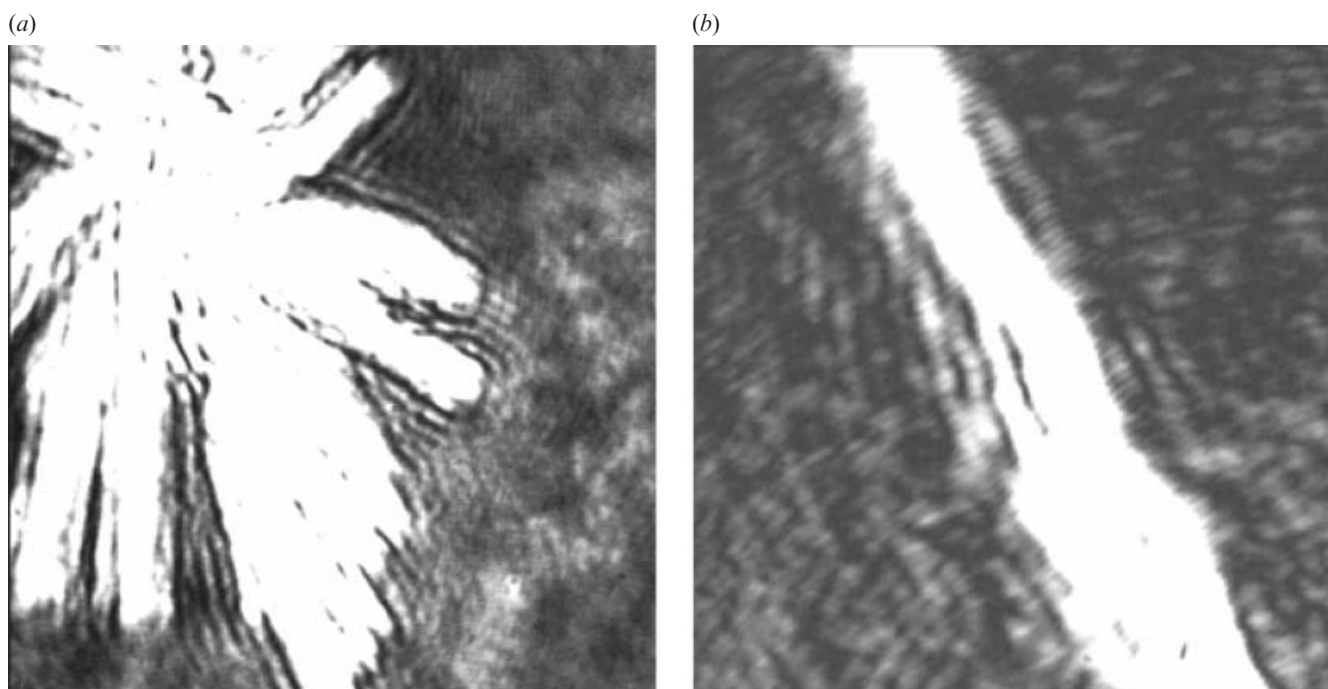


Figure 11. BAM images of Langmuir films formed of (a) 12CB at  $A=0.25 \text{ nm}^2$  and (b) PCH9 at  $A=0.15 \text{ nm}^2$ . The area of images is  $0.35 \times 0.30 \text{ mm}^2$ .

increases when the benzene ring is replaced by the cyclohexane ring. The detailed analysis of the  $\pi$ - $A$  isotherm shapes for the mesogens under investigation gives some evidence that only smectogenic compounds can form regular multilayers on the air-water interface.

The morphology of the Langmuir films has been monitored by Brewster angle microscopy. BAM images for nematogenic compounds have a different appearance to those of smectogens (8CB, 9CB and 10CB). Whereas for smectogens, only optically flat domains were found, the Langmuir films of nematogens were characterized by the existence of 3D droplet-like domains beyond the collapse point (4CB, 5CB, PCH $n$  series) or at the end of the plateau region (6CB, 7CB). The behaviour of the latter liquid crystals appears to indicate the existence of some groups of molecules (similar to cybotactic groups in the bulk [16]) in 6CB and 7CB monolayers, which are early precursors of the smectic order in the next members of the homologous series. Thus, the study of BAM images has confirmed the suggestion from  $\pi$ - $A$  isotherm shapes analysis, that the organization of the liquid crystal molecules in Langmuir films can to some extent be correlated with the type of mesophase that they form in the bulk.

#### Acknowledgements

This work was supported by Poznań University of Technology Research Project No. PB 64-016/2004-BW.

#### References

- [1] M.F. Daniel, O.C. Lettington, S.M. Small. *Thin solid Films*, **99**, 61 (1983).
- [2] J. Xue, C.S. Jung, M.W. Kim. *Phys. Rev. Lett.*, **69**, 474 (1992).
- [3] M.N.G. De Mul, J.A., JR. Mann. *Langmuir*, **10**, 2311 (1995).
- [4] M.N.G. De Mul, J.A., JR. Mann. *Langmuir*, **11**, 3292 (1995).
- [5] M.C. Friedenberg, G.G. Fuller, C.W. Frank, C.R. Robertson. *Langmuir*, **10**, 1251 (1994).
- [6] D. Janietz. *Handbook of Surfaces and Interfaces of Materials*, Vol. 1, edited by H.S. Nalwa (Academic Press), pp. 423-446 (2001).
- [7] T. Martyński, R. Hertmanowski, D. Bauman. *Liq. Cryst.*, **29**, 99 (2002).
- [8] G.L., JR. Gaines. *Insoluble Monolayers at Liquid-Gas Interface* (New York: Interscience) (1996).
- [9] K. Czupryński. *Destabilization of Orthogonal Smectic Phases*, Habilitation Dissertation (in Polish), Warsaw (1995).
- [10] D. Hoenig, D. Moebius. *J. phys. Chem.*, **95**, 4590 (1991).
- [11] T. Martyński, R. Hertmanowski, D. Bauman. *Liq. Cryst.*, **28**, 437 (2001).
- [12] A. Biadasz, T. Martyński, R. Stolarski, D. Bauman. *Liq. Cryst.*, **31**, 1639 (2004).
- [13] R. Hertmanowski, A. Biadasz, T. Martyński, D. Bauman. *J. mol. Struct.*, **646**, 25 (2003).
- [14] K.A. Suresh, A. Bhattachryya. *Langmuir*, **13**, 1377 (1997).
- [15] G. Roberts. *Langmuir-Blodgett Films* (New York: Plenum Press) (1990).
- [16] A. De Vries. *Mol. Cryst. liq. Cryst.*, **10**, 31 (1970).